THE EFFECT OF NITROGENEOUS CONCENTRATE FROM SYNTHETIC CRUDES ON ASPHALT BLENDS

by

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FINAL REPORT

Work on this project was conducted under the auspices of
Canada Centre for Mineral and Energy Technology,
Energy, Mines and Resources Canada

DSS FILE NUMBER : 03SQ.23440-5-9132
DSS CONTRACT SERIAL NUMBER : OSQ85-00150
NRS SCIENTIFIC AUTHORITY : Dr. H. SAWATZKY

AUG 19 1986

PETRO-CANADA PRODUCTS
RESEARCH AND DEVELOPMENT CENTRE
SHERIDAN PARK, ONTARIO

38pp
MICROMEDIA

March, 1986

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EXECUTIVE SUMMARY

This work was undertaken to determine the effects on physical properties and characteristics of asphalt cement when nitrogen concentrates from synthetic crudes are blended into paving asphalts.

A literature review was carried out which indicated that only limited data, in the current state-of-the-art, is available on the subject. The information available, however, revealed that nitrogen-rich compounds extracted from shale oil were effective for use as additives in asphalt-aggregate mixtures to enhance resistance to moisture damage. Further investigations indicated that such compounds also have potential for use as asphalt rejuvenator to restore desired viscoelastic properties of aged asphalts.

Large size nitrogen concentrate samples were prepared by extraction from Raw Syncrude Gas Oil and Suncor Coker Gas Oil. An extensive blending and testing program was carried out to investigate the effects on the asphalt physical properties and characteristics. A total of 16 asphalt samples were prepared and analyzed taking into account 2 types of nitrogen extracts, 2 base asphalt crude sources, and 3 penetration grades, including oxidized and straight run materials. Asphalt blends examined contained nitrogen concentrates ranging between zero and 19%. Various tests were performed for determination of physical properties, temperature susceptibility, chemical composition and infrared spectroscopy analysis. Test data were compared to standard control paving asphalts.

The results of this investigation identified 3 commercial paving application areas in which such nitrogen extracts may be effectively utilized. These are:

1. as blending components in limited quantities in paving asphalt cements,
2. as asphalt antistripping agents for use in asphalt-aggregate mixtures to enhance resistance to moisture type damages, and
3. as asphalt rejuvenators for pavement recycling, to restore desired properties of aged asphalts.

The study concluded that the inclusion of the nitrogen compounds has, in general, the effects of lowering the overall asphalt qualities, as indicated by data on physical properties. Therefore, the utilization as a blending component in paving asphalts can be feasible only:

1. if the quality of the base asphalt significantly exceeds minimum spec. requirements;
2. if in small quantities so that spec. products can be made.

The study also concluded that further investigations should be carried out to reach firm conclusions regarding extent of use and optimum utilization in the 3 identified paving application areas.

Five recommendations on future development needs are made which may be summerized as follows:

1. Explore Full Utilization Potential for Extracts as Blending Components in Paving Asphalts: This lab study should assess potential use over a wider range of asphalt base materials and manufacturing process. It should also explore possible utilization in various paving application areas, including asphalt cements, emulsions and cutbacks.

2. Evaluate Effects on Asphalt-Aggregate Mixture Characteristics: This lab study should examine the effects of incorporating nitrogen extracts on design and engineering characteristics of asphalt-aggregate mixtures. Overall engineering merits/ demerits of such inclusions should be identified and assessed.

3. Evaluate Implications on Long Term Pavement Performance: This lab study should identify long-term pavement performance implications associated with utilization of nitrogen compounds into paving asphalts. In particular, the effects on pavement permanent deformation, fatigue cracking, moisture damage resistance, asphalt ageing resistance and low temperature stiffness behaviour should be evaluated and fully understood.

4. Evaluate Potential Use of Extracts as Anti-Stripping Agents: This study should evaluate effectiveness of nitrogen extracts from synthetic crudes as anti-stripping agents in asphalt aggregate mixtures. The evaluation should include other commercially known anti-stripping additives and non-treated asphalt samples for comparisons.

5. Evaluate Potential Use as Asphalt Rejuvenators: This study should determine relative quality requirements and investigate effectiveness of the nitrogen extracts as asphalt rejuvenators in asphalt pavement recycling mixtures to restore desired viscoelastic properties of the aged asphalts. Other commercially known asphalt rejuvenators should be included for comparison purposes.

TECHNICAL STAFF CONTRIBUTIONS

Technical contributions were made by many staff members at the Petro-Canada Research and Development Centre, including Messrs. L.W. Beauchamp, R.J. Bernais, R.J. Cameron, D.H. Cho, P. Dotchin, B.B. Galvez, D. Kulawic, J.M. McCann, W.M. Meston, G.B. Myall and M.H. Vandal. Dr. J. Chmielowiec, Messrs. R.R. Deutscher, L.J. Miller and D.V. Rasmussen, provided technical consultations. Mr. Nabil I. Kamel, P.Eng., Senior Research Engineer, Asphalt was the principal investigator and the project manager who assumed overall responsibility for the completion of this research program.

THE EFFECT OF NITROGENEOUS CONCENTRATE FROM SYNTHETIC CRUDES ON ASPHALT BLENDS

1. BACKGROUND AND OBJECTIVES

Nitrogeneous components in synthetic crudes are undesirable because they deactivate catalysts that are required for upgrading of these crudes to transportation fuels. Methods have been/are being developed for separating these components rather than by costly hydrotreating. In the case of heavy fractions, these nitrogeneous concentrates represent significant amounts of material. These concentrates can be subjected to severe treatment to recover valuable hydrocarbon products, but they might possess unique utilization properties. One such possibility could be the incorporation of these concentrates into paving asphalt blends.

This project was proposed in response to DSS request number 03SQ.23440-5-9132. The overall objective of the work was to evaluate the effects on physical properties of paving asphalt cements when nitrogeneous concentrate compounds, extracted from synthetic crudes, were blended into asphalts.

The specific objectives of the work were as follows:

1) To carry out a literature search and obtain relative information on the subject of nitrogeneous compounds in asphalts.

2) To carry out a large scale separation of nitrogeneous concentrated fractions from two synthetic crude gas oils.

3) To determine various physical characteristics and properties of the obtained nitrogeneous concentrates.

4) To prepare samples of 85-100 pen paving asphalt blends containing various levels of nitrogeneous concentrates and to determine characteristics and physical properties of both the original and blended asphalts.

5) To assess and analyze the test data obtained and determine the effects of nitrogeneous concentrate compounds on the characteristics and physical properties of the paving asphalt blends.

6) To make recommendations on future development work requirements.

2. LITERATURE SEARCH

The literature search conducted revealed that limited data and information is available on the use of nitrogeneous concentrates in paving asphalts. The body of this information has primarily been developed by H. Plancher, J.C. Petersen, and others of the Western Research Institute, Laramie, Wyoming, U.S.A. The work has almost entirely concerned itself with the evaluation of a basic nitrogen concentrate obtained from experimental refining of shale oil added in a small percentage to conventional petroleum asphalt-aggregate mixtures to improve pavement resistance to moisture damage.

The performance of asphalt pavement is greatly affected by the moisture in the system. Pavement engineers and designers have for many years recognized the detrimental effects of moisture and/or repeated freeze-thaw cycles on pavement performance. Moisture actions cause debonding at asphalt-aggregate interface, leading to pavement failures such as asphalt stripping, surface ravelling and pavement disintegration. Early work in Wyoming [1-3] studied bonding and debonding of asphalt components-aggregate surfaces from a chemical and mechanistic viewpoint. Results from these investigations indicated that certain nitrogen-containing molecules naturally present in asphalt might be involved in reducing the sensitivity of the asphalt-aggregate mixtures to moisture-induced damage. Infrared spectrometric and elemental nitrogen analysis [3-6] of asphalt components removed by hot pyridine extraction from previously benzene-extracted aggregates,

showed that nonpyrrolic nitrogen might, in part, be responsible for an increased resistance of the asphaltic pavements to moisture-induced damage.

Plancher et al, during the development of a water susceptibility test (WST) to indicate the susceptibility of asphalt-aggregate mixtures to repeated freeze-thaw cycles, found that WST briquets prepared from pyridine-pretreated aggregates were highly resistant to moisture damage [2]. Further investigation [7] utilizing a basic nitrogen concentrate obtained as a byproduct from experimental refining of shale oil, and a 342-382°C (648-720°F) shale oil distillate indicated that shale oil asphalt-aggregate mixtures were more resistant to moisture damage than petroleum-derived mixtures. Addition of 0.5 percent of a basic nitrogen concentrate to a petroleum asphalt-aggregate mixture greatly reduced its susceptibility to moisture damage. Additional studies conducted at Texas A&M University [8,9] and in Wyoming [10,11] further indicated that pyridine-type nitrogen in asphalts reduced the effects of moisture damage in asphalt pavements. These studies indicated that shale oil contains significant amounts (1.3 wt.%) of pyridine-type homologs.

Another area investigated by Plancher et al was the ability of nitrogen-rich shale oil fractions to disperse asphaltenes in oxidatively-aged asphalts, in evaluation of their potential use as recycle agents for aged petroleum asphalts. Pavement rehabilitation by recycling of old asphalt pavements has increased dramatically in the last few years throughout the USA and Canada. In this type of pavement reconstruction, asphalt rejuvenating agents are added to aged asphaltic pavements to restore desired viscoelastic properties to the embrittled asphalt binder. Plancher and Petersen [12] reported that nitrogen-containing components from shale oil showed potential as additives for rejuvenating aged asphalt. Their study compared the asphaltene dispersion ability of various additives through a time-settlement test. In their comparisons, the most effective additive was a basic nitrogen concentrate obtained from residue of distillation of a hydroteated crude shale oil. They concluded that this concentrate dispersed asphaltenes in aged asphalts better than did other commercial additives considered in their study such as Cyclopave, Paxole 1009, Ashland 100 and Dutrex 739.

Properties of the shale oil basic nitrogen concentrate used in Plancher et al work is shown in Table 1. The shale oil basic nitrogen concentrate was obtained as a hyproduct by Suntech, Inc., Marcus Hook, PA, during the experimental refining of shale oil produced by the Occidental vertical-modified in situ process [13]. The crude shale oil was first hydrotreated by Suntech to reduce the nitrogen content from 1.5 to 0.5 wt.% and then topped to 281°C by distillation. A portion of the distillation residue (4,826 L) was treated with 2.25 wt.% anhydrous hydrochloric acid (HCl) in a glass-lined reactor at 43°C and 55.2 kPa to precipitate the hydrochloride salts of the nitrogen compounds. The salts were thermally decomposed at 300°C to liberate the HCl and yield the shale oil nitrogen concentrate. Total yield based on feed material was 13.3 wt.%.

TABLE 1

PROPERTIES OF SHALE OIL BASIC NITROGEN CONCENTRATE FROM STREAM CLEANUP DURING EXPERIMENTAL REFINING OF SHALE OIL

Gravity, °API	16.0
5% boiling point, °C	297
95% boiling point, °C	524
Carbon, wt.%	84.03
Hydrogen, wt.%	11.06
Nitrogen, wt.%	3.97
Chlorine, wt.%	0.045

In summary, the Wyoming work investigated the use of a basic nitrogen concentrate from shale oil as an antistripping agent to enhance bond at asphalt-aggregate interface and as an asphalt rejuvenator to restore desired viscoelastic properties of aged asphalt. The nitrogen concentrate was added to the asphalt-aggregate mixture and all stripping or debonding tests were performed on the mixture. The work, however, presented no data to indicate any direct comparisons or to identify the effects on physical properties of paving asphalts with the shale oil nitrogen concentrate additive.

3. PREPARATION OF NITROGEN CONCENTRATE SAMPLES

Preparation of the nitrogen concentrate samples was done by extraction in accordance with a method developed by Gulf Canada [14] in a previous contract, "The Impact of Problematic Components on Synthetic Crude Processing". The extractions were carried out with equal amounts of dimethyl sulphoxide (DMSO) containing 6% water. The extraction process is summarized in Figure 1.

Two starting materials were used to produce the 2 samples of the required nitrogeneous concentrate compounds. These were Raw Syncrude Gas Oil (RSGO) and Suncor Coker Gas Oil (SCGO). Yield obtained on concentrate was 3.4% for the RSGO and 5.6% for the SCGO.

4. MATERIALS CHARACTERIZATION AND ANALYSIS

4.1 Analysis of Base Materials

Infrared spectra analyses were carried out for the two starting gas oil materials. In addition a distillation was obtained on the DMSO to determine impurities, if any. The results on analyses of feed materials are shown in Tables 2 and 3. Table 4 shows data on physical characteristics of the DMSO as provided by the manufacturer of the material.

4.2 Analysis and Characterization of the Nitrogen Concentrates

The 2 nitrogen concentrate samples obtained ex SCGO and RSGO were extensively tested for material characterization, physical property determinations, compound composition analysis, infrared spectroscopy analysis and distillation. The results are summarized in Table 5.

As can be seen, each nitrogen concentrate sample provided distinctive characteristics. The sample ex Suncor has significantly less carbazole and carbazole nitrogen contents, as would be expected. It also displays higher metal and ash percentages, significantly higher material viscosity, i.e. solid at room temperature, and a relatively higher flash point if compared with the extract ex Syncrude. The nitrogen concentrate ex Suncor coker gas oil is

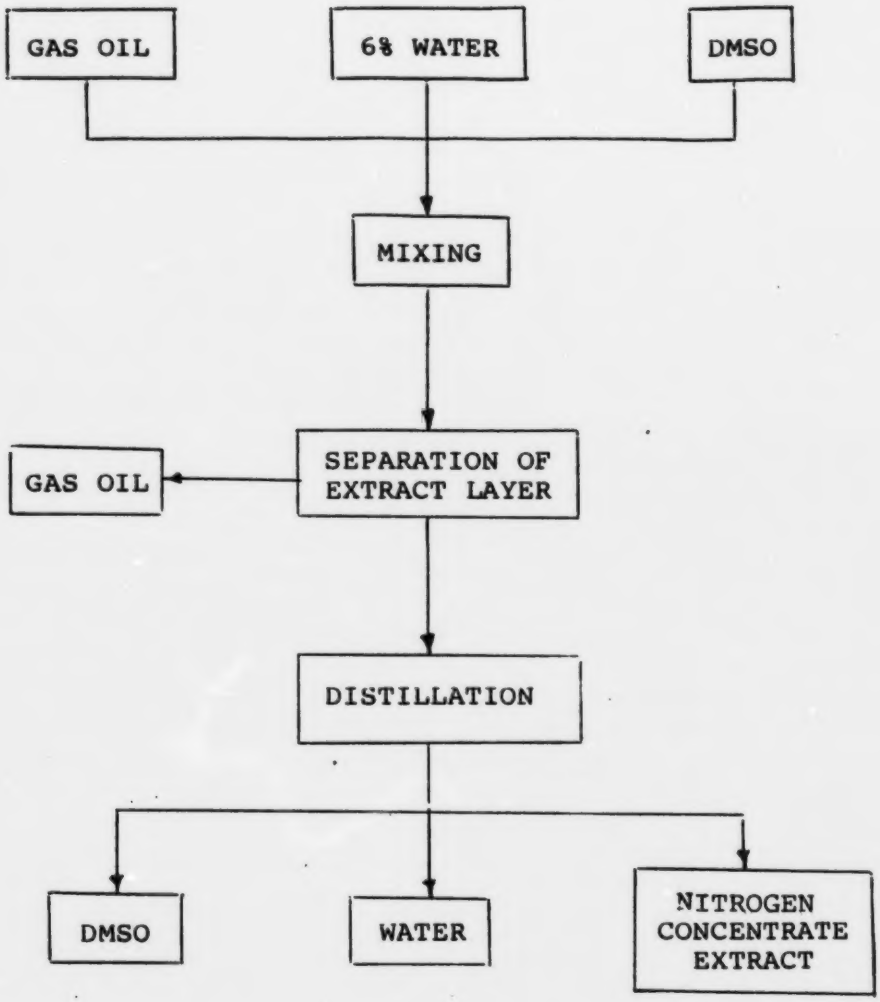


FIGURE 1: FLOW CHART SHOWING PROCESS FOR OBTAINING REQUIRED NITROGEN CONCENTRATE EXTRACT.

TABLE 2

INFRARED SPECTRA ANALYSIS OF THE GAS OIL FEEDS

	Feed (1) Suncor Coker* Gas Oil	Feed (2) Raw Syncrude Gas Oil
Sample Number	D85-81	D85-107
Carbazole, % w/w	0.64	0.65
Carbazole, N ppm	536	545
Alco OH ppm	0.34	N.D.

* IR scan indicated evidence for olefinic structure in Suncor Coker Gas Oil sample.

TABLE 3

DMSO DISTILLATION

Total Recovery	99.89%
Residue	0.11%

TABLE 4

SUMMARY OF MATERIAL PROPERTIES OF THE DMSO
- provided by Manufacturer*

Name	Dymethyl Sulfoxide
Formula	$(CH_3)_2SO$
Boiling Point, °C	189
Vapor Density (Air = 1)	2.7
Vapor Pressure (mm Hg)	0.37
Water Solubility	Complete
Appearance	Colorless liquid
Flash Point, °C	95
Melting Point, °C	18.5
Specific Gravity	1.1
Percent Volatile	100.0
Evaporation Rate (ether = 1)	greater than 1

*Fisher Scientific Company, Chemical Manufacturing Division, Fair Loan, N.J.

also less in aromatics content but it displays a significantly higher asphaltene content as shown by the compound separation analysis. Distillation analysis and carbon number distribution curves obtained on the extract ex Raw Syncrude Gas Oil are shown in Table 6 and in Figures 2 and 3.

It is interesting to compare characteristics of the nitrogen concentrates extracted from SCGO and RSGO with those presented by Plancher and Petersen [12] on the basic nitrogen concentrate from shale oil. As can be seen in Table 7, the basic nitrogen concentrate from shale oil has a relatively higher nitrogen content than obtained for the samples ex Suncor and Syncrude gas oils. The shale oil's basic nitrogen concentrate sample also shows higher carbon and hydrogen contents and displays higher boiling points.

In summary, it would appear that the high nitrogen content in the Syncrude and the Suncor extracts make them both attractive for evaluation as antistripping agents. In addition, the Syncrude extract should further be evaluated as an asphalt rejuvenator agent for pavement recycling; and both extracts may have the potential to be utilized as blending components in the production of paving asphalts.

TABLE 5

CHARACTERISTICS OF NITROGENEOUS CONCENTRATES

Sample Number	Suncor Sample 55-0970	Syncrude Sample 55-0986
A) Physical Properties		
Specific Gravity	1.10	1.09
C content, %	81.37	80.12
H content, %	6.98	8.21
N Content, %	1.51	1.96
S Content, %	8.34	7.74
Heptane Insol, wt.%	30.0	5.30
Toluene Insol, wt.%	4.9	0.13
Soluble in $ClCHCCl_2$, %	97.8	99.8
Metal, PPM		
V	3.9	0.2
Ni	8.2	3.3
Cu	37.2	2.1
Ash, Wt.%	1.018	0.054
Viscosity at 60°C, cSt	496	25
Viscosity at 135°C, cSt	68	2.68
Softening Point, °C	43	N/A (liquid at room temp.)
Flash Point, °C	192	172
Penetration, 25°C, 100 g, 5 sec.	84	>400
B) Compound Separation		
Asphaltenes, nC_5, %	54.0	24.6
Saturates, %	0.9	1.0
Aromatics, %	40.6	70.1
Polars, %	4.5	4.3
Recovery, %	95.3	89.4
C) Spectroscopy Analysis (Infrared)		
Carbazole, %	3.9	10.2
Carbazole, N ppm	3260	8600
D) Distillation Analysis	N/A	See Table 6 & Figures 2 & 3

TABLE 6: PETRO-CANADA PRODUCTS, RESEARCH & DEVELOPMENT CENTRE
GC DISTILLATION & CARBON NUMBER DISTRIBUTION DATA: GC379

Sample ID: 550986.01 RAW SYNCRUDE GAS OI Date:12/17/85 20:08:08

%OFF	C	F	%OFF	C	F	%OFF	C	F	%OFF	C	F
IBP	156	312	25	340	645	50	376	708	75	418	784
1	158	317	26	342	648	51	377	711	76	420	788
2	164	326	27	344	651	52	379	713	77	422	792
3	174	345	28	345	653	53	380	716	78	424	796
4	190	373	29	347	656	54	381	719	79	426	800
5	245	473	30	348	659	55	383	721	80	429	804
6	279	534	31	350	662	56	384	724	81	431	808
7	287	549	32	351	664	57	386	726	82	433	812
8	292	558	33	353	667	58	387	729	83	436	816
9	297	566	34	354	669	59	389	732	84	438	821
10	301	575	35	356	672	60	391	735	85	441	826
11	306	582	36	357	674	61	392	738	86	444	831
12	309	588	37	358	677	62	394	741	87	447	836
13	312	594	38	360	679	63	396	744	88	450	842
14	315	599	39	361	682	64	397	747	89	453	848
15	318	605	40	362	684	65	399	750	90	457	854
16	321	609	41	364	687	66	401	753	91	461	861
17	323	614	42	365	689	67	403	757	92	465	869
18	325	618	43	366	691	68	404	760	93	469	877
19	328	622	44	368	694	69	406	763	94	474	885
20	330	626	45	369	696	70	408	767	95	479	895
21	333	631	46	370	698	71	410	770	96	486	907
22	335	635	47	371	701	72	412	773	97	495	922
23	337	638	48	373	703	73	414	777	98	508	946
24	339	642	49	374	705	74	416	781	99	531	988
									FBP	552	1026

C#	DEG:C		%	SUM	C#	DEG:C		%	SUM	C#	DEG:C		%	SUM
1- 3	IBP	-15	0.00	0.00	25	396	407	6.17	69.45	47	558	563	0.07	99.67
4	-15	8	0.00	0.00	26	407	417	5.11	74.57	48	563	568	0.07	99.74
5	8	54	0.03	0.04	27	417	426	4.27	78.83	49	568	572	0.05	99.78
6	54	85	0.01	0.05	28	426	435	3.84	82.67	50	572	577	0.05	99.84
7	85	115	0.00	0.05	29	435	444	3.41	86.08	51	577	581	0.03	99.87
8	115	140	0.00	0.05	30	444	453	2.83	88.91	52	581	586	0.04	99.91
9	140	162	1.69	1.74	31	453	462	2.38	91.30	53	586	590	0.03	99.94
10	162	185	2.07	3.80	32	462	470	1.88	93.17	54	590	594	0.03	99.97
11	185	206	0.62	4.42	33	470	477	1.41	94.58	55	594	598	0.03	100.00
12	206	225	0.32	4.74	34	477	485	1.27	95.86	56	598	602	0.00	0.00
13	225	244	0.25	4.99	35	485	492	0.87	96.73	57	602	606	0.00	0.00
14	244	262	0.20	5.19	36	492	499	0.66	97.39	58	606	610	0.00	0.00
15	262	279	0.83	6.02	37	499	506	0.49	97.88	59	610	614	0.00	0.00
16	279	294	2.38	8.40	38	506	512	0.34	98.22	60	614	617	0.00	0.00
17	294	309	3.57	11.97	39	512	519	0.33	98.55	61	617	619	0.00	0.00
18	309	323	4.95	16.92	40	519	525	0.23	98.79	62	619	624	0.00	0.00
19	323	337	6.11	23.03	41	525	531	0.20	98.99	63	624	627	0.00	0.00
20	337	350	8.12	31.15	42	531	537	0.17	99.16	64	627	630	0.00	0.00
21	350	362	8.64	39.79	43	537	542	0.12	99.29	65	630	633	0.00	0.00
22	362	374	9.05	48.84	44	542	547	0.11	99.40	66	633	637	0.00	0.00
23	374	385	7.70	56.53	45	547	553	0.11	99.51	67	637	640	0.00	0.00
24	385	396	6.76	63.29	46	553	558	0.08	99.60	68+	640	643+	0.00	0.00

Injection @:12/17/85 19:02:32 Inst:16 File#:OS32:LH526800.RAW/L
Int.Std.(Wt%)= 0.00 Window: 8.00- 20.00
Calib. ID:CA16DE17 Area/100: 20999. Blname: Analyst:MOHAMME
Start/End Delta 0.0000 / 0.0001 Data Start/End Time 0.00/ 43.26
Start/End Inhibit 0.00 0.00 Data Set:16 GCD ON HP5880A (INST:16)

FIGURE 2

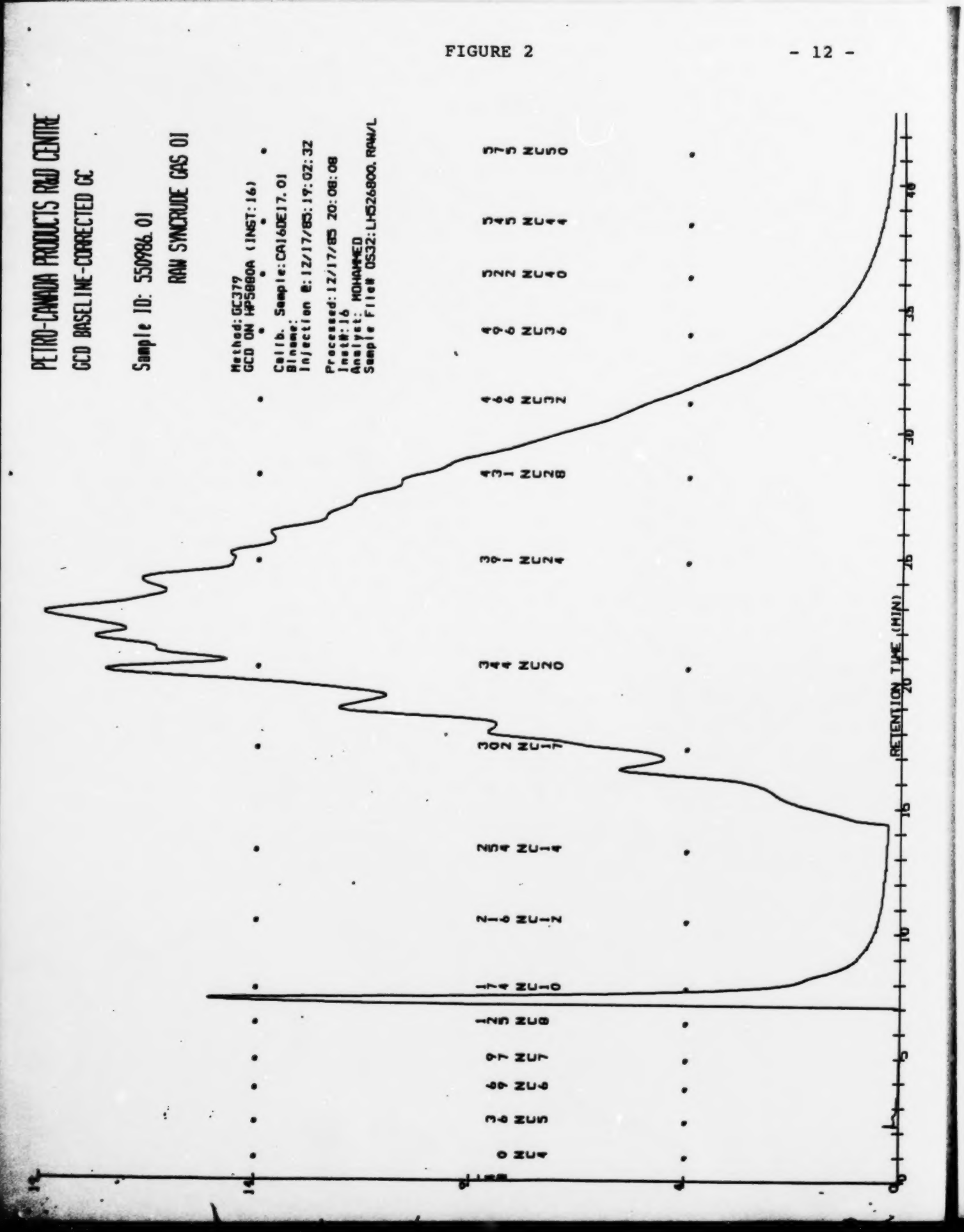

PETRO-CANADA PRODUCTS R&D CENTRE
GCD BASELINE-CORRECTED GC
Sample ID: 550986.01
RAW SYNCRUDE GAS 01
Method: GC379
GCD ON HP5880A (INST:16)
Calib. Sample: CA16DE17.01
Blname:
Injection @: 12/17/85 19:02:32
Processed: 12/17/85 20:08:08
Inst#: 16
Analyst: MOHAMMED
Sample File# 0532: LH526800.RAW/L
RETENTION TIME (MIN)

FIGURE 3

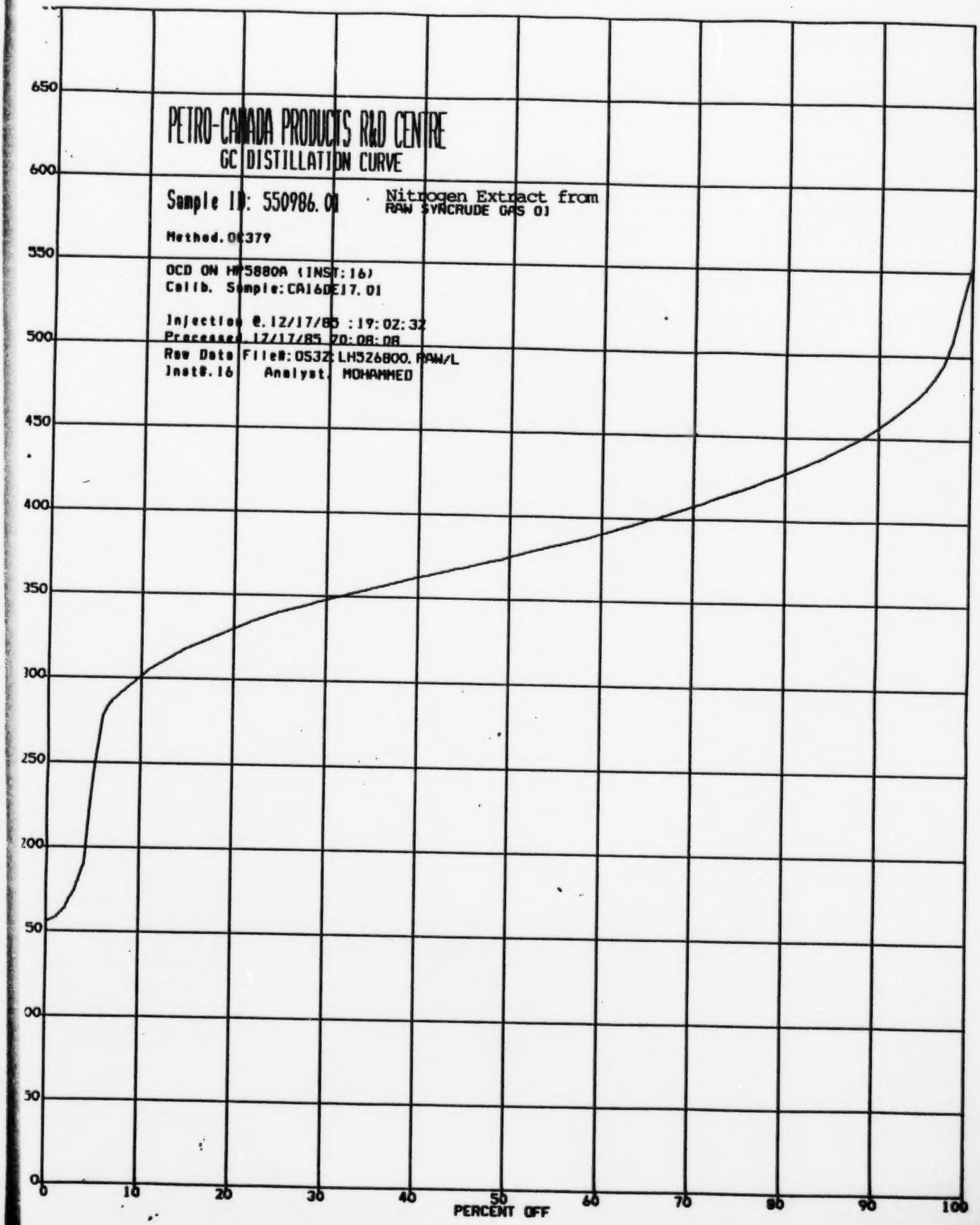

PETRO-CANADA PRODUCTS R&D CENTRE
GC DISTILLATION CURVE
Sample ID: 550986.01
Nitrogen Extract from
RAW SYNCRUDE GAS OIL
Method.OC379
OCD ON HP5880A (INST:16)
Calib. Sample:CA16DE17.01
Injection @.12/17/85 :19:02:32
Processed.12/17/85 20:08:08
Raw Data File#:0532:LH526800.RAW/L
Inst#.16 Analyst. MOHAMMED
650
600
550
500
450
400
350
300
250
200
150
100
50
0
0
10
20
30
40
50
60
70
80
90
100
PERCENT OFF

TABLE 7

PROPERTIES OF VARIOUS NITROGEN CONCENTRATES

	Basic Nitrogen Concentrate		
	Shale Oil	Suncor G.O.	Syncrude G.O.
5% Boiling Point, °C	297	N/A	250
95% Boiling Point, °C	524	N/A	480
Carbon, wt.%	84.03	81.47	80.12
Hydrogen, wt.%	11.06	6.98	8.21
Nitrogen, wt.%	3.97	1.51	1.96
S content, wt.%	?	8.34	7.74

5. BLENDING WITH ASPHALTS

An extensive blending and testing scheme, designed for a full-range evaluation on the effects of blending the nitrogen concentrates in paving asphalts was carried out. A total of 16 asphalt and asphalt blend samples were prepared and analyzed, taking into account the following variables:

a) two nitrogen concentrate types
   two asphalt crude sources, and
c) three asphalt penetration grades
   - 85-100 pen as a blending base asphalt with SCGO extract
   - 20-30 pen oxidized material as a blending base asphalt
   - 50-60 pen oxidized and straight run materials as blending base asphalts.

Asphalt blends were made containing nitrogen concentrates ranging between zero and 19% and various tests were carried out for determination of physical properties, temperature susceptibility, and compound composition. In addition, infrared spectroscopy analyses were done on all asphalt base materials, the 2 nitrogen concentrates and the various asphalt blends made. Results are summarized in Tables 8 and 9.

It should be noted that appropriate warning should be given to personnel handling extract material at high temperatures. In our case, during the analysis of the concentrate ex. Suncor coker gas oil, the asphalt technologist complained of a "strong and unpleasant" odor which caused a mild upset stomach. Due to the high viscosity of the extract, it handles like asphalts, i.e. solids at room temperature. It is normally heated to enable proper handling. The odor was somewhat controlled by maintaining the temperature under 125°C.

TABLE 8

PROPERTIES OF BASE ASPHALTS AND ASPHALT BLENDS USING EXTRACT EX. SYNCRUDE GAS OIL

Materials	Nitrogen	Asphalt Base Materials				Asphalt Blends				Control Asphalts	
Crude Source	Extract	LLOYDMINSTER		S. SASKATCHEWAN		LLOYDMINSTER		S. SASKATCHEWAN		LLOYD.	S. SASK.
Pen. Grade	Ex	20-30	50-60	20-30	50-60	85-100	85-100	85-100	85-100	85-100	85-100
	Syncrude	Oxid.	St. Run	Oxid.	Oxid.	Blend	Blend	Blend	Blend	St. Run	St. Run
Sample Number	55-0986	85-3260	55-0928	55-887-2	55-931-2-7	55-0987	55-0990	55-0988	55-0989	55-0926	84-3737
%N Concentra'n in Blend	100%	NIL	NIL	NIL	NIL	19%	5%	15%	8%	NIL	NIL
a) Physical Properties											
Kinematic Vis, 135°C, cSt	2.68	6452	491	2515	540	487	316	332	314	333	321
Absolute Vis, 60°C, Pa.S	0.24	707820	3045	164505	9306	2695	1253	2278	1592	1337	1302
Ductility, 25°C, 5 cm/min.	N/A	415	127	16	48	56	>150	61	>150	139	133
Solubility, $ClCHCCl_2$,%	99.8	99.9	99.8	99.9	99.9	99.7	99.7	99.8	99.7	99.8	99.9
Heptane Insoluble, wt.%	5.30	29.02	17.3	28.6	23.8	25.8	17.2	26.6	22.7	16.3	16.2
Flash Point, COC, °C	172	272	324	268	304	242	285	243	274	320	318
Softening Point, °C	N/A	81	49	70	57	48	44	46	46	43	44
Thin Film Oven Test:											
% Wt. Loss		-0.05	-0.08	-0.12	-0.11	-0.96	-0.81	-1.45	-0.90	-0.08	-0.06
Pen, 25°C, 100 g, 5 s		21	40	22	35	34	52	41	49	61	54
% of Original Pen		100	75	85	64	34	58	42	51	66	64
b) Temperature Susceptibility:											
Pen-Vis. Number, PVN		+1.6	-0.6	+0.8	-0.4	+0.1	-0.7	-0.5	-0.6	-0.5	-0.6
Penetration Index, PI		+2.5	-1.0	+1.3	+0.5	+0.1	-1.6	-0.5	-0.5	-1.6	-1.6
Penetration, 100 g 5 s:											
0°C		3	2	4	5	13	3	10	8	4	5
5°C		5	5	6	8	14	8	15	13	9	8
10°C		7	8	8	12	22	14	23	20	16	15
15°C		10	15	13	20	35	27	37	33	31	25
20°C		14	28	18	31	57	47	56	55	46	43
25°C	Too Soft	21	53	26	55	100	89	98	97	92	85
30°C		29	95	35	72	140	141	145	129	138	122
c) Compound Composition:											
% Asphaltenes, nC_5	24.6	38.4	25.1	38.0	34.5	32.4	25.3	33.1	29.9	23.8	24.2
% Saturates	1.0	15.9	12.3	13.1	13.6	14.0	12.0	12.6	13.1	13.9	12.1
% Aromatics	70.0	33.5	44.8	37.4	38.2	39.8	47.4	41.5	44.5	44.5	48.7
% Polars	4.3	12.2	17.8	11.5	13.7	13.8	15.3	12.8	12.5	17.8	14.8
% Total Recovery	89.4	99.5	100.0	99.8	97.3	100.0	97.8	97.5	99.9	98.6	99.2
d) Infrared Spectra Analysis											
% Carbazole content	10.2	0.63	0.79	0.62	0.70	1.94	1.23	1.92	1.37	0.7	0.76
% Carbazole N, ppm	8600	525	664	516	585	1622	1031	1609	1108	584	640

TABLE 9

PROPERTIES OF BASE ASPHALTS AND ASPHALT BLENDS USING EXTRACT EX. SUNCOR COKER GAS OIL

Materials	Nitrogen	Asphalt Base Materials		Asphalt Blends				Control Asphalts	
Crude Source	Extract	LLOYDMINSTER	S. SASKATCHEWAN	LLOYDMINSTER		S. SASKATCHEWAN		LLOYD.	S. SASK.
Pen. Grade	Ex Suncor	85-100	85-100	85-100	85-100	85-100	85-100	85-100	85-100
Sample Number	55-0970	55-0926	84-3737	55-0972	55-0973	55-0974	55-0975	55-0926	84-3737
%N Concentra'n in Blend	100%	NIL	NIL	5%	15%	5%	15%	NIL	NIL
a) Physical Properties									
Kinematic Vis, 135°C, cSt	68	333	321	311	269	309	285	333	321
Absolute Vis, 60°C, Pa.S	572	1337	1302	1226	585	1275	944	1337	1302
Ductility, 25°C, 5 cm/min.		139	133	32	28	52	43	139	133
Solubility, $ClCHCCl_2$,%	97.8	99.8	99.9	99.2	99.0	99.8	99.7	99.8	99.9
Heptane Insoluble, wt.%	30.0	16.3	16.2	18.1	23.9	19.8	24.1	16.3	16.2
Flash Point, COC, °C	192	320	318	314	306	311	298	320	318
Softening Point, °C	43	43	44	43	43	44	43	43	44
Thin Film Oven Test:									
% Wt. Loss	-	+0.08	-0.06	-0.34	-1.18	-0.38	-1.14	+0.08	-0.06
Pen, 25°C, 100 g, 5 s	-	61	54	53	54	54	60	61	54
% of Original Pen	-	66	64	55	44	61	54	66	64
b) Temperature Susceptibility:									
Pen-Vis. Number, PVN		-0.5	-0.6	-0.6	-0.6	-.07	-0.7	-0.5	-0.6
Penetration Index, PI	-1.7	-1.6	-1.6	-1.5	-1.0	-1.5	-1.0	-1.6	-1.6
Penetration, 100 g 5 s:	-	4	5	6	7	6	8	4	5
0°C	-	9	8	8	10	8	10	9	8
5°C	-	16	15	15	19	16	18	16	15
10°C	-	31	25	27	31	26	31	31	25
15°C	-	46	43	49	61	47	52	46	43
20°C	84	92	85	97	122	89	111	92	85
25°C	-	138	122	147	174	135	162	138	122
30°C									
c) Compound Composition:									
% Asphaltenes, nC_5	54.0	23.8	24.2	24.4	25.7	26.0	26.9	23.8	24.2
% Saturates	0.9	13.9	12.1	13.4	12.9	12.5	13.0	13.9	12.1
% Aromatics	40.6	44.5	48.9	45.6	44.6	46.1	43.1	44.5	48.7
% Polars	4.5	17.8	14.8	16.6	16.8	15.4	17.1	17.8	14.8
% Total Recovery	95.3	98.6	99.3	98.8	97.2	98.4	99.8	98.6	99.3
d) Infrared Spectra Analysis									
% Carbazole content	3.9	0.70	0.76	0.86	1.17	0.92	1.23	0.7	0.76
% Carbazole N, ppm	3260	584	640	720	984	768	1030	584	640

6. ANALYSIS AND DISCUSSION OF THE ASPHALT TEST RESULTS

Based on the test data presented in Tables 8 and 9, the following observations are made:

6.1 Effects on Physical Properties:

a) When oxidized base materials are used, the asphalt blends containing nitrogen concentrate showed viscosity values at 135°C comparable to control asphalts. However, when straight run base materials are used, the high temperature viscosities of the blends showed lower values. This is not unexpected, since the starting viscosities of the oxidized base asphalts are much higher than those for straight run materials.

The data on high temperature viscosity from Tables 8 and 9 are shown graphically in Figures 4 and 5. As can be seen the asphalt viscosity declined rapidly as the amount of nitrogen concentrate increased in the blend. With the Syncrude nitrogen extract, Figure 4, both the Lloydminster and the S. Saskatchewan asphalts exhibited similar viscosity decline rates; whereas with the Suncor extract, Figure 5, the rate of decline in viscosity differed from one asphalt source to the other.

b) Figure 5 also shows the effects on asphalt penetration with the addition of the Suncor extract. It is very apparent that the asphalt penetration of the blend increases as the amount of nitrogen extract increases. The trend remains the same for both asphalt base materials examined. This penetration trend is unusual, since the penetration of the Suncor extract is less than that of the base asphalts. It is normal, in such situations, for the penetration of the resultant blend to decline rather than to increase. This phenomenon, however, is not unique and has been observed with special blends in other investigations; but, it is of particular interest in this case because the Suncor extract might, if this trend remains true with low pen aged asphalts, have the potential to be used as a rejuvenator.

c) In most cases with both Suncor and Syncrude nitrogen extracts, asphalt blends examined showed a drop in ductility values at 25°C relative to control samples. In some cases, particularly with the Suncor extract, the drop appeared very dramatic even with addition of only 5% of the extract material.

The ductility test provides a measure of the tensile and cohesion of the material at the specified test temperature.

d) All blends satisfied the spec. requirements for solubility in $ClCHCCl_2$ of greater than 99%. All were comparable with control asphalts.

e) All blends showed flash points above the spec. requirement of 230°C for 85-100 pen grade. However, blends with the Syncrude extract and oxidized asphalts showed significantly lower flash points than control asphalts. This is due to the lower flash points of both the oxidized base asphalts and the Syncrude extract.

f) All blends showed equivalent or slight increase in softening point relative to control asphalts.

g) All blends showed significant increase in the loss of asphalt mass after the Thin Film Oven Test (TFOT) compared with the control samples. They also showed significant drop in retained penetration after the test. Blends containing higher than 5% of the Syncrude nitrogen extract failed to meet the requirements of 0.85% max. loss in mass and/or the 45% min. of original pen retained after the TFOT.

The TFOT results for the various asphalt blends with Suncor extract are shown graphically in Figure 6. As can be seen, both asphalt base types showed consistent increases in % wt. loss with increasing the amounts of nitrogen concentrate in the blend. The results of the % original pen retained after the test also showed consistent trends for both asphalt base types.

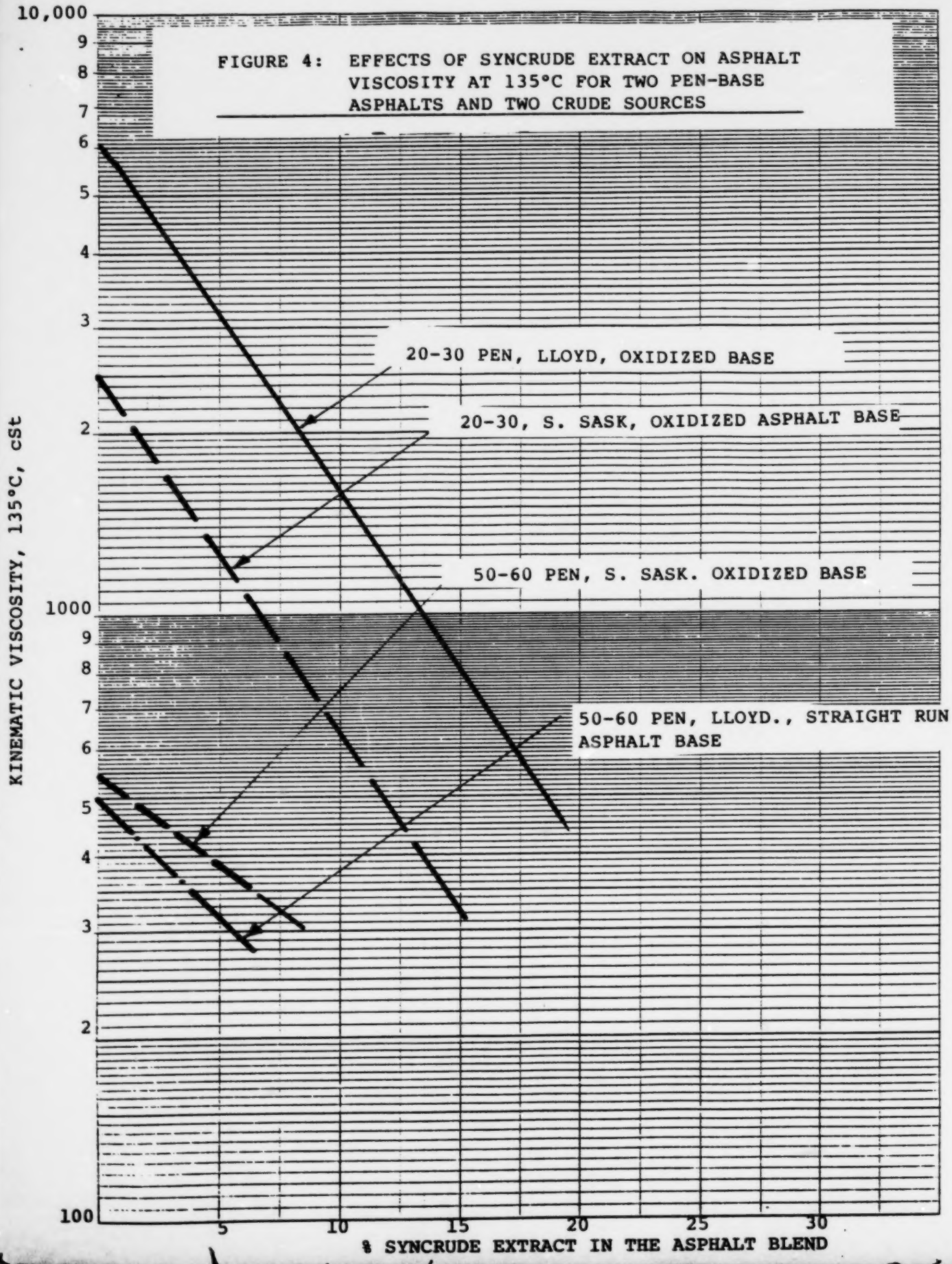


FIGURE 4: EFFECTS OF SYNCRUDE EXTRACT ON ASPHALT VISCOSITY AT 135°C FOR TWO PEN-BASE ASPHALTS AND TWO CRUDE SOURCES

FIGURE 5: EFFECT OF CONCENTRATE EX SUNCOR COKER GAS OIL ON ASPHALT VISCOSITY AND PENETRATION FOR TWO CRUDE SOURCES

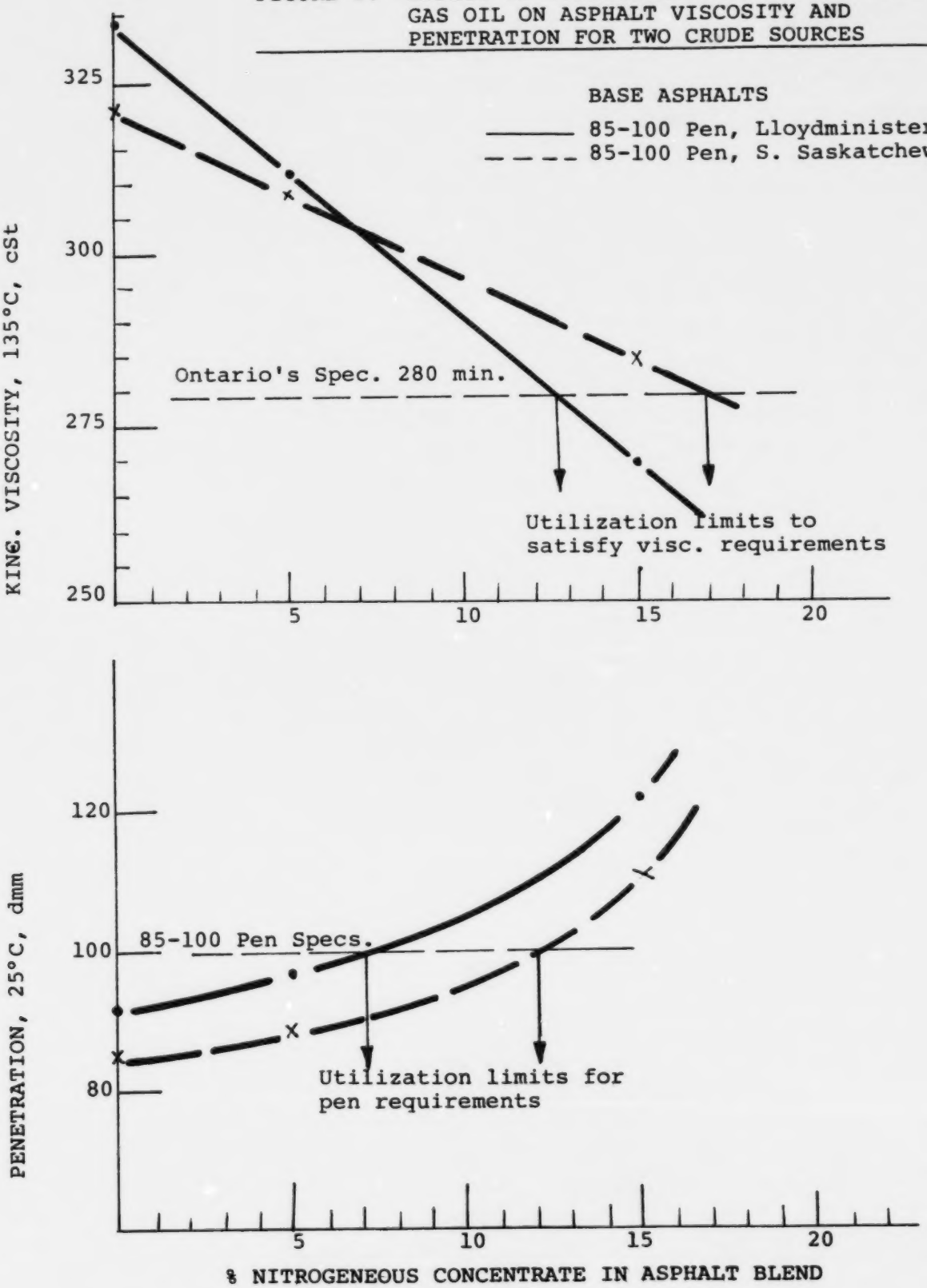
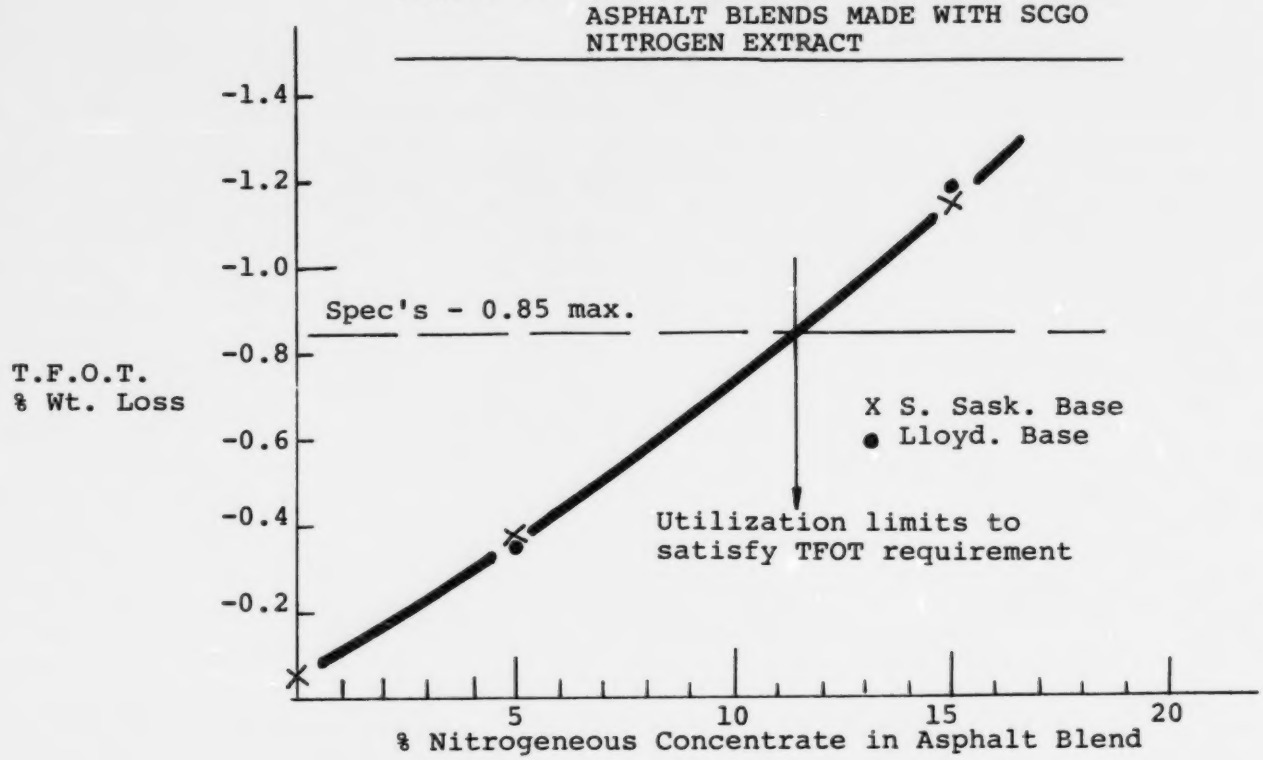
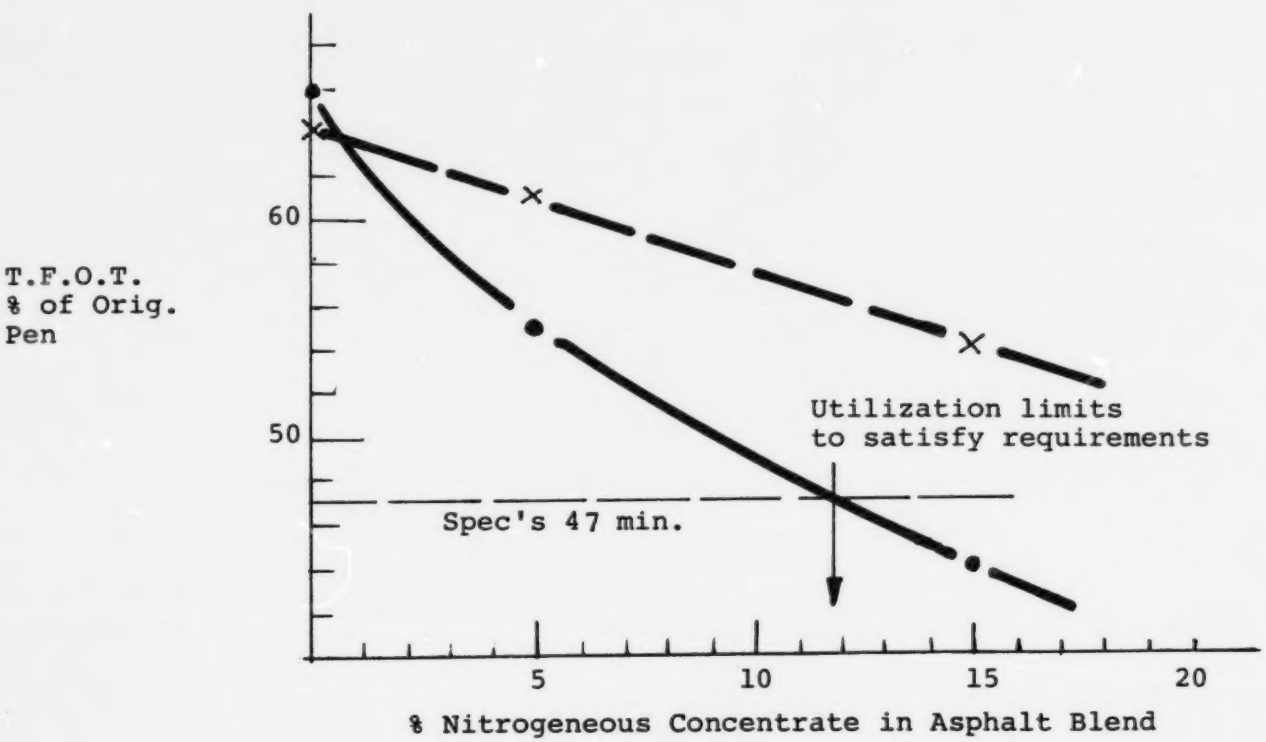


FIGURE 6: THIN FILM OVEN TEST RESULTS FOR ASPHALT BLENDS MADE WITH SCGO NITROGEN EXTRACT





The S. Saskatchewan blends showed higher retained pen figures than did the Lloydminster blends. Both, however, showed persistent decline in percent pen retained with increasing the amounts of nitrogen concentrate in the asphalt blend.

The Thin Film Oven Test is an important specification test which simulates ageing or hardening conditions approximating those that occur during manufacturing of hot asphalt mixtures. The asphalt weight loss and the asphalt hardening after the thin film oven test occur due to evaporation of low molecular weight fractions. Both tests are used as indicatives of the as-constructed paving asphalt quality. A higher asphalt quality is generally indicated by a very small percent weight loss and a high percent penetration retained after the TFOT. Current specifications require a max. weight loss of 0.85% and a minimum of 47% penetration retained for 85-100 pen paving asphalts.

The TFOT results on the asphalt blends containing nitrogenous concentrate, in all cases, showed decline in the asphalt cement qualities relative to control asphalts. In cases where the Syncrude concentrate was used in quantities exceeding 5% in the blend, the TFOT results failed to meet the specification limits for 85-100 pen paving asphalt cement.

In summary, the physical property tests indicate that inclusion of the nitrogen concentrate compounds in the asphalt results in lowering the overall quality of the paving asphalt. It is feasible, however, for both types of nitrogen extracts examined to be blended in paving asphalts in limited quantities, so that asphalt specification products can be made. For example, see limits illustrated on Figures 5 and 6.

6.2 Effects on Temperature Susceptibility

Temperature susceptibility of all the asphalt blends and asphalt base materials were evaluated by both the Pen-Vis Number (PVN) and the Penetration Index (PI) methods [15,16,17] In addition, standard asphalt penetration tests were performed on all samples over a wide range of temperatures (covering zero to 30°C) as shown in Tables 8 and 9.

The PVN results suggest that, in general, the asphalt blends containing the nitrogen concentrates show medium temperature susceptibility values similar to that obtained for the control asphalt materials. One exception is noted in the case of

Syncrude extract with the 20-30 pen oxidized base asphalt. In this case the PVN results suggest the temperature susceptibility of the resultant asphalt blend is low, i.e. superior to that of the control asphalts.

The PI method gave somewhat different results. It showed that in the case of Syncrude extract, one blend only (using straight run 50-60 pen Lloyd base) provided temperature susceptibility value that is similar to the control asphalts, while the other 3 blends provided values indicating superior properties. In the case of Suncor extract, similar trend is also given. The PI results indicate the 2 blends containing 15% extract show somewhat better temperature susceptibility qualities; while the 2 blends containing 5% extract display low-temperature characteristics similar to control asphalts.

The various penetration-temperature results obtained on the various blends are shown graphically in Figures 7 and 8. The results indicate the following:

a) in the case of Syncrude extract, the blends with oxidized base asphalts show improved temperature susceptibility over those of the control asphalts. The blend with straight run base material shows temperature susceptibility similar to those of the control asphalts.

b) all the blends containing Suncor extract show similar temperature susceptibility to those observed for the control asphalts.

6.3 Effects on Asphalt Chemical Composition

a) With the Syncrude extract no significant changes in composition are noted for the asphalt blends in comparison to the control asphalts, except for the high asphaltene content for blends with oxidized asphalt base, which would be expected.

b) With the Suncor extract slight increases in asphaltene content are observed due to the high asphaltene content in the Suncor extract.

6.4 Effects on the Infrared Spectroscopy Analysis

All asphalt blends showed significant increases in % carbazole and carbazole N content relative to the control asphalts. As would be expected, the blends containing the Syncrude nitrogen concentrate showed significantly higher concentrations of carbazole and carbazole Nitrogen contents than those blends made with the Suncor extract.

FIGURE 7: PENETRATION-TEMPERATURE RELATIONSHIPS FOR VARIOUS ASPHALT BLENDS MADE WITH SYNCRUDE EXTRACT

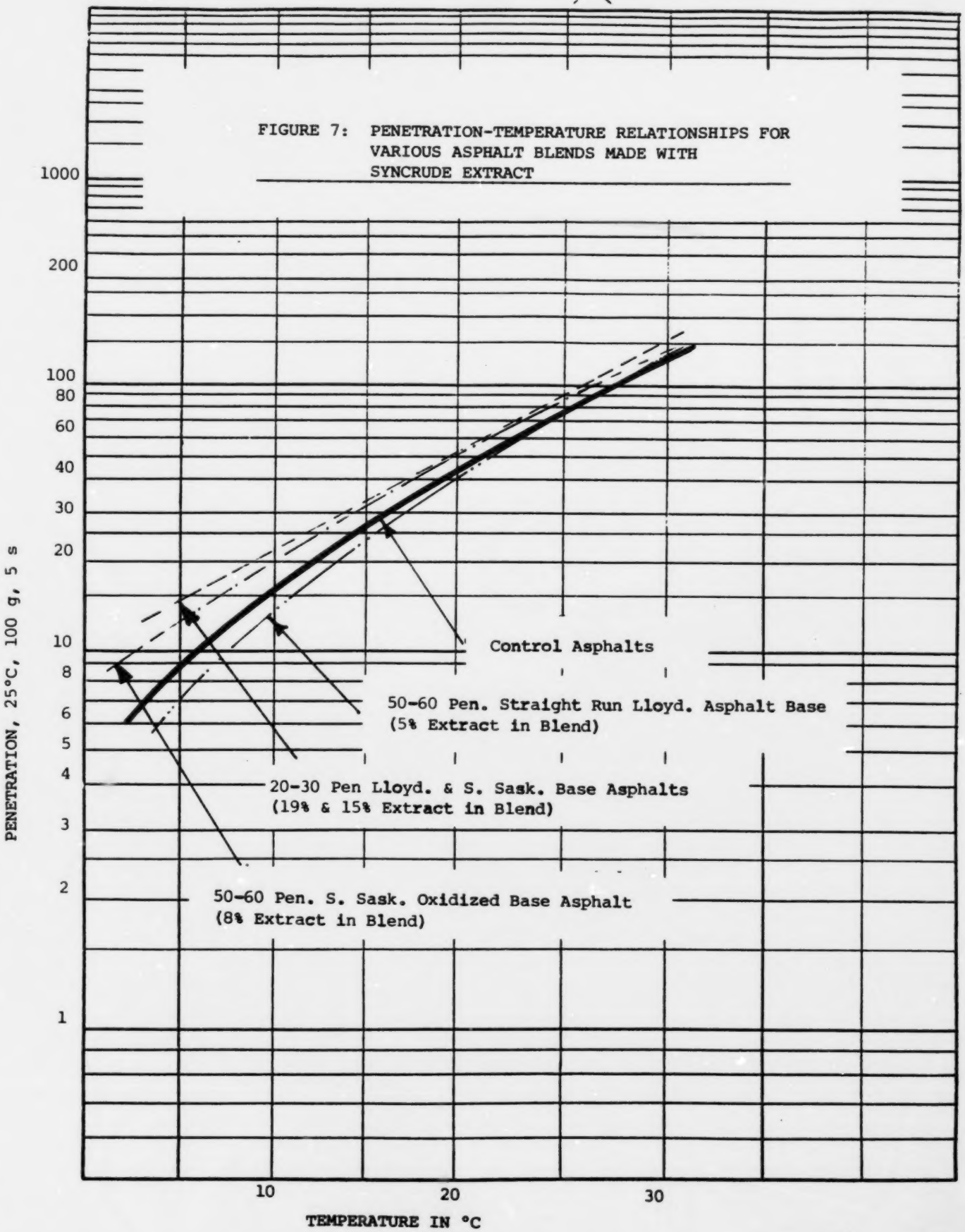
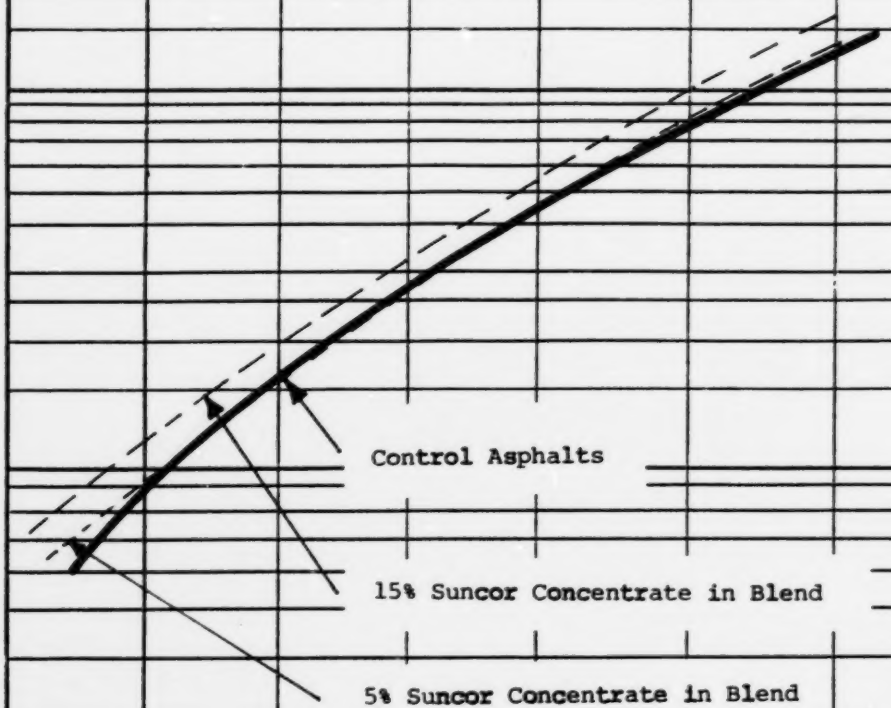


FIGURE 8: PENETRATION-TEMPERATURE RELATIONSHIPS FOR VARIOUS ASPHALT BLENDS MADE WITH SUNCOR EXTRACT



7. SUMMARY AND CONCLUSIONS

The objectives of this project were: to carry out a literature search on use of nitrogen compounds in paving asphalts, to extract large samples of nitrogen concentrates from 2 synthetic crudes, namely raw Syncrude and Suncor Coker gas oils, to prepare test samples of 85-100 pen paving asphalts containing various levels of nitrogen extract and to test and analyze all base and test samples to determine the effects on asphalt physical properties and characteristics due to blending the nitrogen compounds.

The literature search indicted that no data are available identifying the effects on physical properties of asphalt blends containing nitrogen compounds from synthetic crudes. However, such nitrogen-rich compounds extracted from shale oil were investigated as additives in asphalt-aggregate mixtures and showed potential for use as antistripping agents and as rejuvenators to restore desired viscoelastic properties of aged asphalts.

Two large-size nitrogen concentrate samples were prepared by extraction from the 2 designated crudes. Yields obtained were 3.4% for Syncrude and 5.6% for Suncor materials. Preliminary analysis of the two nitrogen extracts and comparisons with the nitrogen concentrate ex. shale oil indicated potential for use in 3 application areas:

a) as blending components in paving asphalts,
b) as asphalt antistripping agents in asphalt-aggregate mixtures, and
c) as asphalt rejuvenators for pavement recycling.

Further specialized investigation directed into the above 3 areas would have to be carried out before firm conclusions can be made regarding suitability, extent and optimum utilization in these areas.

The test results on 16 asphalt blends containing nitrogen extracts, in amounts between zero and 19% by weight, indicated the following effects on asphalt physical properties and characteristics:

a) asphalt viscosity declines rapidly as the amount of concentrate increases in the blend. This implies that only a small and

limited quantity can be used as blending components in paving asphalts. Optimum quantity will depend upon the viscosities of base materials, sources of crudes employed, and the end product specifications desired.

b) Asphalt ductility showed large drops relative to control asphalts.

c) Asphalt softening point showed equivalent or slight increased values. This should pose no concern for blends within the limits examined.

d) Asphalt flash points showed decreased values but all samples tested were above minimum spec. requirements.

e) Thin Film Oven Test indicated significant increases in loss of asphalt mass and a large drop in retained penetration after the test. These imply that only limited quantities can be used as blending components in paving asphalt pool. No concern in the other application areas, i.e. as rejuvenator and as antistripping agents.

f) Solubility in $ClCHCCl_2$ showed values above minimum requirements for paving asphalt specifications.

g) Asphalt temperature susceptibility evaluations indicated equivalent or improved properties when oxidized base asphalts are employed.

h) Significant increases in nitrogen content for all asphalt blends confirmed the potential for use in improving asphalt-stripping resistance in asphalt-aggregate mixtures.

In the overall, it is concluded that the inclusion of nitrogen concentrates in the asphalt results in reducing the qualities of the paving asphalt. Both nitrogen extracts examined, however, can feasibly be utilized as blending components in paving asphalts if used in limited small quantities.

8. RECOMMENDATIONS ON FUTURE DEVELOPMENT NEEDS

8.1 Explore Full Utilization Potential as Blending Components in Paving Asphalts

The results of this investigation showed, in general, encouraging results for utiliztion of both nitrogen extracts as blending components in paving asphalts. A more comprehensive study is needed to determine potential use over a wider range of asphalt base materials (i.e. wider sources of asphalts and for manufacturing process employed) and to explore potential utilization in various paving applications including paving asphalt cements, asphalt emulsion and asphalt cutbacks. Particular attention should be given to binder properties which showed sensitive changes with the nitrogen concentrate additions. These include high temperature viscosity, absolute viscosity, penetrations, Thin Film Oven Test including ductility determinations on residue after the TFOT (the latest is a spec. item in some regional areas).

8.2 Evaluate Effects on Asphalt-Aggregate Mixture Characteristics

The end use of any paving asphalt is in an asphalt-aggregate mixture system. The mixture characteristics may be affected by the introduction of an additive and, therefore, evaluation of mixture characteristics is essential to understand the total effects that may be taking place. A study is needed which will carry out standard asphalt-aggregate mix designs, formulate and prepare asphalt-aggregate mixtures, with and without nitrogen compounds, prepare Marshall test briquettes, and test mixture characteristics, Marshall design properties, i.e. stability, flow, voids, etc., mix modulus of elasticity M_R at various temperature levels, examine stripping resistance and carry out asphalt recovery tests, and examine asphalt ageing properties in comparison with control asphalts employed.

8.3 Evaluate Long Term Pavement Performance Implications

Evaluation of pavement performance under repeated, full-scale, heavy loads is an important part of an assessment of long term implications of incorporating nitrogen compounds into paving asphalts. These performance implications, both negative and/or positive, should be understood and evaluated as part of the overall assessment in utilization of the nitrogen compounds. These should

include effects on the following prime pavement performance factors:

- effects on pavement permanent deformation and rutting resistance
- effects on pavement fatigue cracking resistance
- effects on pavement moisture-damage resistance for both open and dense graded type mixes
- effects on asphalt aging resistance
- effects on low temperature stiffness performance (low temperature pavement crackings).

The Petro-Canada R&D Centre is equipped with a unique pavement test pit for simulation and testing of long term pavement performance. A study is needed which will design an experimental program aimed to answer the above pavement performance concerns for pavements incorporating nitrogen concentrates and compare the results with control asphalt pavements.

8.4 Evaluate Potential Use of Extracts as Anti-Stripping Agents

This study will include preparation and testing of asphalt-aggregate mixtures to evaluate effectiveness of the nitrogen extracts as antistripping agents. The study should include known commercial antistripping additives and non-treated asphalt samples for comparisons.

8.5 Evaluate Potential Use as Asphalt Rejuvenators

It has been indicated that the Syncrude extract has a good potential for use as an asphalt rejuvenator agent. A further study is needed which will prepare and test extract-asphalt blends to determine appropriate binder properties, particularly as a rejuvenator, and to confirm effectiveness in this vital application area. Other known commercial asphalt rejuvenators should also be included in the study for comparison purposes.

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